The Drop Weights of Twenty Non-associated Liquids and the Molecular Weights Calculated for them

DISSERTATION

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE FACULTY OF PURE SCIENCE IN COLUMBIA UNIVERSITY IN THE CITY OF NEW YORK

BY

GARABED K. DAGHLIAN

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Professor J. Livingston R. Morgan suggested and directed this work. The author begs to tender to Professor Morgan his sincere thanks for the assistance, advice and encouragement accorded him during the work.

G. K. D.

CONTENTS

OBJECT OF THE INVESTIGATION

The object of this work has been to apply the principles arrived at by former workers in drop weights to further non-associated liquids. They proved, first, that the drop weight of a liquid, measured under proper conditions, is proportional to its surface tension; and consequently can be substituted in place of surface tension in Eotvos' formula as modified by Ramsay and Shields.

$$\gamma\left(\frac{M}{d}\right)^{2/3} = k\,(t_c - t - 6)$$

where γ stands for surface tension as measured by capillary rise, M for molecular weight, d for density at temperature, t of the liquid, and t_c the critical temperature. Second, they proved that this method is a great deal more accurate than surface tension method.

APPARATUS AND METHOD

The apparatus used has been devised and improved into its present form by Professor Morgan. For a detailed description see Jour. Am. Chem. Society, March, 1911.

Its essential part consists of a **U** shaped tube with a capillary bore, one end of which is carefully ground to a diameter of 5.8 *mm.*, and terminates with a smooth circular surface perpendicular to the axis of the tube, and the bore of 0.2 *mm.* being in the centre. The other leg of this syphon tube dips in a small vessel which contains the liquid worked with, so that by applying gentle suction at the other end the liquid rises in the tube and is syphoned over into another small weighing vessel, which is fitted air-tight at the tip, forming drops. The apparatus is so designed that these two small vessels can be removed and replaced readily; so allows work at different temperatures; and is so arranged that it can be in a water bath at the desired temperature. These baths are heated with the vapor of boiling ether or chloroform or can be cooled by allowing tap water to run through them.

The liquid at all times is under perfect control, being regulated by means of a rubber bulb which is connected by capillary rubber tubing to the weighing vessel through the ventilation tubes.

The **U** shaped siphon tube which is called the *"tip"* is cleaned before starting a new liquid by running through it potassium dichromate solution and sulphuric

acid, water, alcohol, ether, and dry air. The supply vessel is then half filled with the liquid and a drop allowed to form and hang for five minutes, after the constant temperature is attained, to saturate the vessel with the vapor, and then a definite number of drops (15, 25, 30) is run into the weighing vessel. This with its contents is then weighed after the apparatus is removed from the bath. A number of such determinations are made. Then a number of determinations, *"blanks,"* are made with only 5 drops; but the sixth drop is allowed to hang without falling long enough to make the time of this determination equal to that of the other with more drops. In this way any evaporation through the ventilation tubes, or condensations, or evaporation from the drops before falling, or evaporation back to the hanging drop, etc., are made equal in the two sets of determinations. By subtracting the average weight of one set from that of the other we get the weight of number of drops equal to the difference of those taken in the two. And that gives us the weight of single drop at the temperature of observation.

Sometimes, when the liquid has a very high boiling point, at low temperature, it is only necessary to use the weight of the empty vessel as blank.

Weight of a single drop is given in milligrams and is indicated by w.

$w\left[\frac{M}{d}\right]^{2/3}$ is called the *molecular drop function* and we will indicate it by $f(M)$.

STANDARDIZATION OF THE APPARATUS

We mean by this the testing to see if a tip of this size, 5.8 *mm.*, will give uniform results with the test liquids as tips of different sizes with which work has been done before; and at the same time to determine the constant of this particular tip. The test liquids are aniline, benzene, pyridene and quinoline. A number of determinations have been made with each one of these at two temperatures. Weight of single drop has been obtained, and k has been calculated for each liquid at both temperatures from equation

$$f(M) = k(t_c - t - 6)$$

in which w and t have been measured and observed, and d and t have been taken from former determinations.

Table I gives the equations for densities, the critical temperatures (by Higgins), and the molecular weights of the test liquids as has been used in the following calculations:

TABLE I

		t_c	*Mol. Wt.*
Aniline	$d_t = 1.038797 - 0.0008605\ t$	425.8	93.00
Benzene	$d_t = 0.900214 - 0.0010659\ t$	288.4	78.00
Pyridene	$d_t = 1.001500 - 0.0010018\ t$	347.0	79.00
Quinoline	$d_t = 1.109894 - 0.0008034\ t$	520.4	129.00

Carbon tetrachloride is one of the usual test liquids. But on account of the great size of this tip and the very small volume of the drop that liquid was omitted. It is clear that whenever a drop falls abruptly and not by its own weight, the drop weight is too large. Carbon tetrachloride has a very small surface tension and a large density; for this reason the drop falls abruptly and so weighs heavier. The tip being very large, too much liquid in weight is contained in the drop volume for the surface tension of the liquid to be able to hold without breaking. As soon as this breaking takes place before the maturity of the drop, the falling part carries with it apparently part of the liquid which would remain on the surface of the tip as remaining-drop if it had not been snatched unduly. On tips still larger carbon tetrachloride gives proportionately larger values. But on smaller tips it is possible to control the drop as the weight of liquid contained in the drop is not too large for the tension of the bounding surface to break it prematurely.

The experimental values for the test liquids are given in Table II.

TABLE II

	Temp.	Wt. vessel + liquid	Average wt.	Wt. vessel + 5 drops	Average wt.	Average temp.	Drop wt.
Aniline	34.30	11.0954(10)	11.0956	10.6440(0)	10.6440	34.28	45.16
	34.20	11.0960 »					
	34.35	11.0960 »					
	34.30	11.0950 »					
Benzene	36.05	11.0871(15)	10.0869	10.7954	10.7955	36.15	29.14
	36.05	11.0868 »		10.7956			
	36.35	11.0868 »					
	59.575	11.0472 »	11.0471	10.7883	10.7883	59.64	25.88
	59.525	11.0474 »		10.7882			
	59.525	11.0467 »					
Pyridine	23.025	11.2548(15)	11.2549	10.8484	10.8483	22.93	40.66
	22.750	11.2550 »		10.8482			
	23.125	11.2544 »					
	22.825	11.2553 »					
	58.325	10.6389(25)	10.6386	9.9346	9.9343	58.39	35.215
	58.425	10.6384 »		9.9340			
	58.400	10.6385 »					
Quinoline	22.375	10.4846(15)	80.4846	9.7525(0)	9.7525	22.33	48.81
	22.275	10.4846 »					

In Table III are given the results of calculation from these experimental values.

TABLE III

	M	$t°$	w	d	f(M)	k
Aniline	93	34.3	45.16	1.0093	921.20	2.3898
Benzene	78	36.15	29.14	0.8617	587.47	2.3857
		59.54	25.88	0.8368	532.06	2.3874
Pyridene	79	22.93	40.66	0.9875	759.31	2.3872
		58.39	35.215	0.9430	674.23	2.3858
Quinoline	129	22.33	48.725	1.09195	1175.17	2.3882

The meaning of k for any one liquid is this: If we work with one of the liquids at different temperatures, and calculate molecular drop function for each temperature, when we plot a curve taking these for ordinates and for abscissas t_c -t-6, then we have a straight line for our curve which makes an angle equal to arc tan k with the axis of x. Moreover if we proceed likewise with other liquids, we get a straight line for each liquid equally inclined to the axis of x, only they intercept the axis of x at different distances from the origin. When f(M) plotted in this way does not give a straight line for the curve, that liquid is called to be *associated.**

The average k is called the constant of the tip. For reason to be mentioned later we will adopt as the constant of this tip k value for benzene which is 2.3866.

In working with these liquids special care had to be exercised with aniline to have it freshly distilled, and also to see that the capillary bore of the tip is washed with ether and dried, by passing dry air through it for 10-15 minutes, between determinations. Otherwise the successive determinations give larger and larger values. When pure, aniline is almost colorless, and standing for even a day causes it to color a little. In all cases the drops were formed fast, then checked before falling, and allowed finally to fall *slowly* and of their own weight. Causing a drop to fall rapidly always gives a heavier drop, for it does not fall of its own weight alone, but is forced out and takes with it more liquid than it should.

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*See also page (12)

TWENTY NEW LIQUIDS

The investigation of twenty new liquids by drop weight method forms the main part of this work. These liquids were of greatest attainable purity. Brombenzene and iodobenzene were specially prepared in the laboratory; diphenyl methane was from Eimer and Amend, redistilled and recrystallized just before the determination was made; isobutylacetate, m-xylene, o-xylene, p-xylene, one sample of mesitylene, bromine and phosphorus trichloride were from Kahlbaum, usually redistilled just before using; while the others, including one sample of mesitylene were especially prepared for this work by the Hoffman and Kropff Chemical Co. (619 Kent Avenue, Brooklyn, N. Y.), and used directly.

Experimental results are given below in Table IV. All the individual results are not given, only those where the determination and the blank were at the same temperature being included in the tables. But the mean of *all* determinations is within a very small error equal to the values given.

TABLE IV

Brombenzene

Temp.	Wt. Vessel + liquid	Average wt.	Wt Vessel + 5 drops	Average wt.	Average temp.	Drop wt.
37.90	11.5863(25)	11.5867	10.8345	10.83485	38.3	37.593
38.40	11.5870 »		10.8352			
31.55	11.5867 »					
59.625	11.5210 »	11.52085	10.8252	10.82495	59.67	34.795
59.700	11.5207 »		10.8247			

Bromine

0	11.4376(15)	11.43803	10.9141	10.91435	0.00	52.368
0	11.4380 »		10.9146			
0	11.4385 »					

Carbon disulphide

20.15	11.1733(15)	11.17337	10.8190	10.81900	20.13	35.437
20.35	11.1718 »		10.8190			
19.90	11.1750 »					

Cymene

18.95	11.0995(15)	11.1009	10.7963	10.79677	18.7	30.413
18.75	11.1015 »		10.7968			
18.35	11.1018 »		10.7972			
59.45	11.0406 »	11,0407	10.7774	10,7774	59.45	26.33
59.45	11,0408 »					

TABLE IV (*Cont.*)

Dimethyl aniline

Temp.	Wt. Vessel + liquid	Average wt.	Wt. Vessel + 5 drops	Average wt.	Average temp.	Drop wt.
21.45	11.2381(15)	11.2380	10.8419	10.84185	21.5	39. 15
21.55	11.2379 »		10.8418			
59.50	11.1684 »	11.1684	10.8196	10.8194	59.5	34.9
59.55	11.1684 »		10.8192			
59.45	11.1689 »		10.8194			
59.50	11.1679 »					

Diphenyl methane

59.05	11.2108(15)	11.2110	10.6440(0)	10.6440	59.0	37.8
59.00	11.2113 »					
58.875	11.2109 »					

Ethyl benzene

20.90	11.1154(15)	11.11545	10.8022	10.8022	21.0	31.325
21.10	11.1155 »					
59.40	11.0528 »	11.0523	10.7846	10.7846	59.5	26.776
59.60	11.0519 »					

Ethyl aniline

35.80	11.2152(15)	11.2152	10.8355	10.8354	35.8	37.98
35.80	11.2150 »		10.8355			
35.80	11.2154 »		10.8352			
58.70	11.1760 »	11.1760	10.8224	10.8225	58.7	35.35
58.70	11.1760 »		10.8224			

Ethylene chloride

34.20	11.1483(15)	11.14843	10.8166	10.81665	34.1	33.178
34.10	11.1484 »		10.8167			
34.07	11.1486 »					
60.00	11.4258(26)	11.4258	10.8404(6)	10.8404	60.0	29.27

Ethylidene chloride

34.125	11.0427(15)	11.04263	10.7822	10.7822	34.10	26.043
34.100	11.0422 »		10.7822			
34.050	11.0430 »					
56.90	11.2097(20)	11.2097	10.8683(10)	10.8683	56.9	22.76

Flourbenzene

9.30	12.8962(20)	12.8962	12.2747 (0)	12.2747	9.3	31.077
9.30	12.8965 »					
9.30	12.8960 »					
34.50	12.9630(25)	12.96316	12.4122	12.4124	34.5	27.537
34.50	12.9631 »		12.4126			
34.50	12.9634 »		12.4125			

TABLE IV (*Cont.*)

Iodobenzene

Temp.	Wt. Vessel + liquid	Average wt.	Wt. Vessel + 5 drops	Average wt.	Average temp.	Drop. wt.
23.5	11.9297 (50)	11.9297	10.1876 (10)	10.1876	23.5	43.55
59.6	10.9270 (30)	10.9270	10.1441 (10)	10.1441	59.6	39.085

Isobutyl acetate

23.8	10.5152 (30)	10.5152	10.0082 (10)	10.0082	23.8	25.35
59.375	10.2991 (25)		9.8680 (5)		59.3	21.55
59.275	10.4075 (30)		9.9766 (10)			

Mesitylene

23.55	11.0844 (15)	11.0844	10.7812	10.7812	23.5	30.32
23.50	11.0844 »		10.7812			
57.20	11·0452 »	11.0446	10.7787	10.7786	57.3	26.60
57.40	11.0440 »		10.7785			

Metaxylene

29.90	10.2095 (15)	10.2095	9.9057	9.9057	24.9	30.38
58.9	10.1529 »	10.1529	9.8888	9.8888	58.9	26.41

Methyl aniline

24.65	10.8230 (25)	10.8231	9.9660	9.9659	24.6	42.86
24.55	10.8232 »		9.9659			
59.7	11.2219 »	11.2218	10.8378	10.8380	59.7	38.38
59.7	11.2217 »		10.8382			

Orthoxylene

23.85	10.2345 (15)	10.23455	9.9144	9.9144	23.85	32.05
23.85	10.2346 »		9.9144			
59.30	10.1756 »	10.1753	9.8965	9.8965	59.4	37.88
59.50	10.1750 »					

Paraxylene

37.9	11.3678 (25)	11.3678	10.7921	10.7921	37.9	30.785
59.2	11.3079 »	11.3081	10.7820	10.78195	59.2	26.308
59.195	11.3083 »		10.7819			

Phosphorus trichloriue

35.57	11.5517 (30)	11.5514	10.9567 (10)	10.9567	35.6	29.73
35.60	11.5515 »		10.9567 »			
35.62	11.5510 »					

Toluene

36.05	11.0809 (15)	11.08085	10.7916	10.7916	36.0	28.925
36.00	11.0808 »		10.7916			
59.1	11.0425 »	11.0423	10.7819	10.78144	59.2	26.075
59.3	11.0421 »		10.7812			

It has been shown by Morgan that the value k'_B found from the equation

$$f(M) = k_B(288.5-t-6)$$

for any one tip, with benzene (where 288.5 is the observed critical temperature), can be used as the standard constant of the tip worked with. And that from this k_B using it in the equation

$$f(M) = k_B(t_c-t-6);$$

for any other liquid, M is shown to be the normal molecular weight of that liquid when the calculated value of t_c from w, M, and d for the new liquid at different temperatures, t, is the same; for the constancy of t_c independent of temperature shows that k_B is also the correct temperature coefficient of the molecular drop function of that liquid, and hence it is non-associated, just as the standard liquid benzene is non-associated.

Further, it is plain that surface tension in dynes per centimeter of any liquid can be calculated directly from drop weight in milligrams at the same temperature by aid of the proportion $\gamma : w = k'_B : k_B$ where k_B is the corresponding value for the surface tension as found from

$$\gamma\left(\frac{M}{d}\right)^{2/3} = k'_B(288.5-t-6)$$

and so by using these two values k'_B and k_B comparisons at different temperatures can be made of drop weight and surface tension.

We can look at this also from the graphical side. It was pointed out that graphical meaning of k is that it is the slope of a certain curve, and that this slope changes in value according to the size of the tip. If we strike a tip of just proper size so that its k is the same as the k obtained from surface tension (which is about 2.12) then drop weights of a liquid from that tip in milligrams is equal to the surface tension of that liquid in dynes per centimeter at the same temperature.

It must be remembered here that drop weight in essence is a more directly experimental value than surface tension by capillary rise, for the former is simply a singly determined weight, while the latter is equal to $\frac{1}{2} r h (d-d')$ where r stands for the radius of a small capillary bore, assumed to be constant, h for the height of the column of liquid rising into the capillary bore, which is burdened with an error of 6-9% due to the volume of the meniscus, and $d-d'$ for the difference of the density of the liquid and density as vapor at that temperature. This, perhaps, will serve to account for the variable results below of surface tension as obtained from capillary rise.

Below in Table V are given the values of the function $f(M)$ and t_c as calculated from drop weights, together with the same values, as far as they can be found in the literature, calculated from capillary rise. Each liquid is taken as a subdivision of Table V, and the molecular weight and the formula for the density as used in the following calculations are given; also the observed t_c. Of the columns the first is the temperature, and the others are in order drop-weight or surface-tension, density, molecular function, and t_c calculated.

TABLE V

1. *Brombenze*, M=156.96, d_t=1.5203—0.001282, t_c=397.0

38.3	37.593	1.4713	845.6	398.6
59.67	34.794	1.4438	792.557	397.8

2. *Bromine*, M=159.84, d_o=3.18718, t_c=302.2

0.0	52.368	3.1872	712.17	304.4
		Ramsay and Aston, k_B=2.12112		
10.6	40.27	3.152	552.08	276.9
46.0	34.68	3.031	487.98	282.1
78.1	29.51	2.917	426.09	285.0

3. *Carbon disulphide*, M=76.14, d_t=1.29215—0.0013025t, t_c=275(*)

20.13	35.440	1.26594	544.05	254.1

4. *Cymene*, M=134.112, d_t=0.862—0.0008044 (t–11.9), t_c=378.6

18.69	30.414	0.85554	883.52	394.9
59.45	26.330	0.82376	785.20	394.5
		Renard and Guye, k_B=2.1108		
11.9	27.98	0.862	809.38	401.3
31.7	26.19	0.846	767.13	401.1
54.8	23.95	0.828	711.65	397.95
74.5	22.16	0.812	667.08	396.5
91.8	20.60	0.798	627.35	395.0
108.9	19.18	0.784	591.04	394.9
117.0	18.45	0.778	571.57	393.7
134.9	16.97	0.762	532.96	393.4
146.5	15.94	0.751	505.48	392.0
163.4	14.60	0.735	469.68	391.9
172.8	13.92	0.726	451.50	392.7

5. *Dimethyl aniline*, M=121.098, d_t=0.9589—0.000825 (t–16.7), t_c=414.45

21.5	39.615	0.95494	999.94	446.5
59.5	34.90	0.92359	900.74	442.9
		Dutoit and Friderich, k_B=2.10124		
22.7	35.31	0.9540	891.5	453.0
43.5	32.81	0.9368	838.6	448.6
76.7	29.24	0.9086	762.5	445.6
99.0	26.80	0.8895	708.3	442.1

(*) also 272.96, 277.63, 271.8, 279.6, 278.05

TABLE V (*Cont.*)

Renard and Guye, k_B=2.1108

10.9	36.27	0.964	909.75	447.9
41.0	33.12	0.939	845.41	447.5
55.0	31.53	0.927	811.76	445.6
78.9	28.84	0.907	753.38	441.8
96.0	27.04	0.892	714.26	440.4
108.8	25.71	0.882	684.25	438.9
126.7	23.91	0.866	644.16	437.9
134.8	23.12	0.858	626.26	337.5
154.0	21.20	0.840	582.87	436.2
165.0	20.18	0.828	560.61	436.6
175.5	19.19	0.822	535.28	435.1

6. *Dephenyl methane*, M=168.1, d_t=1.0126—0.0007914 (t–11), t_c=497

59.0	37.80	0.9745	1171.26	555.8

Dutoit and Friderich, k_B=2.10124

108.3	27.86	0.9209	931.4	557.5
210.2	19.11	0.8438	677.1	538.4

7. *Ethyl benzene*, M=106.08, d_t=0.88316—0.0008333t, t_c=346.4

21.9	31.325	0.86566	772.83	350.8
59.5	26.775	0.83358	681.13	351.3

8. *Ethyl aniline*, M=121.098, d_t=0.9796—0.000831t, t_c=425.4

35.8	37.89	0.9488	862.06	444.90
58.7	35.35	0.9310	907.51	444.96

Dutoit and Friderich, k_B=2.10124

7.4	37.26	0.9738	927.9	455.0
107.8	22.89	0.8886	698.4	446.2
210.0	16.76	0.7996	477.6	443.3

9. *Ethylene chloride*, M=98.95, d_t=1.280149—0.0015277t, t_c= { 288.4 / 289.3 / 283.3

34.1	33.178	1.22805	618.79	299.4
60.0	29.27	1.18850	558.09	299.8

10. *Ethylidene chloride*, M=98.95, d_t=1.206951—0.0015992t, t_c= { 250.0 / 254.5 / 260.0

34.065	26.042	1.1525	506.87	252.5
56.8	22.76	1.1160	452.56	252.5

TABLE V (*Cont.*)

11. *Flourbenzene*, M=96.04, d_t=1.04655—0.001208t, t_c=286.55

9.3	31.077	1.03435	636.80	282.1
34.5	27.537	1.00537	574.62	281.7

12. *Iodobenzene*, M=203.96, d_t=1.8606—001535t, t_c=448.0

23.5	43.55	1.82445	1010.62	453.0
59.6	39.08	1.7691	925.73	453.5

13. *Isobutyl acetate*, M=116.096, d_t=0.8802—0.001055 (t–10), t_c= { 288.3 / 295.8

23.8	25.35	0.86565	664.23	308.1
59.3	21.55	0.82820	581.54	309.0

14. *Mesitylene*, M=120.1, d_t=0.8746—0.00081t, t_c36=7.7

23.5	30.32	0.8656	812.61	370.0
57.3	26.60	0.8282	734.21	370.9

Dutoit and Friderich, k_B=2.10124

7.4	27.92	0.8686	746.1	368.5
108.4	18.47	0.7846	528.9	360.1

Renard and Guye, k_B=2.1108

11.4	28.3	0.866	758.23	376.6
25.1	26.7	0.054	722.05	373.2
36.3	25.84	0.845	703.75	375.7
55.4	23.99	0.829	661.74	374.9
64.8	23.29	0.821	646.60	377.1
74.3	22.20	0.814	619.39	373.8
92.2	20.57	0.798	582.01	373.9
108.9	19.03	0.784	544.83	373.0
127.0	17.43	0.769	509.38	374.3
146.6	15.83	0.752	465.98	373.4
156.2	15.02	0.744	445.30	373.2

15. *Metaxylene*, M=106.08, d_t=0.874—0.000944 (t–10), t_c=345.6

24.9	30.38	0.8599	752.85	346.4
58.9	26.41	0.8271	671.67	346.3

Dutoit and Friderich, k_B=2.10124

15.7	28.97	0.869	714.2	361.6
74.9	22.71	0.814	583.4	358.5
136.7	16.56	0.759	445.8	354.8

TABLE V (*Cont.*)

Renard and Guye, $k_B=2.1108$

10.0	28.88	0.874	707.95	351.4
38.0	26.06	0.849	651.57	352.7
49.0	24.75	0.837	624.47	351.6
63.9	23.25	0.824	592.78	350.7
76.8	21.94	0.812	564.88	350.4
88.0	20.85	0.803	540.82	350.2
99.4	19.74	0.792	516.76	350.2
109.0	18.94	0.784	499.18	351.5
128.3	17.16	0.767	458.93	351.7
136.5	16.43	0.759	442.49	352.1

16. *Methyl aniline*, M=107.08, $d_t=0.9944-0.000801(t-10)$, $t_c=428.6$

24.6	42.86	0.9827	977.78	440.3
59.7	38.38	0.9546	892.68	440.3

Dutoit and Friderich, $k_B=2.10124$

9.9	39.19	0.9947	886.5	437.8
108.5	26.37	0.9128	690.2	443.0
210.8	18.59	0.8227	477.7	444.1

17. *Orthoxylene*, M=106.08, $d_t=0.8932-0.0008425t$, $t_c=358.3$

23.85	32.015	0.8731	785.36	358.9
59.40	27.88	0.8432	701.07	359.15

18. *Paraxylene*, M=106.08, $d_t=0.8801-0.0008468t$, $t_c=344.4$

37.9	28.785	0.8480	720.0	345.6
59.2	26.308	0.8300	667.51	344.9

19. *Phosphorus trichloride*, M=137.38, $d_t=1.61275-0.0013463t$, $t_c=285.5$

35.6	29.73	1.5649	587.24	287.66

Ramsay and Shields

16.4	28.71	1.582	562.3	287.50
46.2	24.91	1.527	499.8	287.80

20. *Toluene*, M=92.064, $d_t=0.8682-0.0009526(t-15.2)$, $t_c=\begin{cases}320.8\\320.6\end{cases}$

36.0	28.925	0.8484	658.57	318.04
59.2	26.075	0.8263	603.75	318.02

Ramsay and Aston, $k_B=2.12112$

15.2	28.18	0.8682	631.0	318.7
46.6	24.60	0.8380	563.9	318.0
78.4	20.93	0.8080	490.8	315.8
132.5	15.53	0.7535	382.2	319.5

TABLE V (*Cont.*)

Renard and Guye, k_B=2.1108

13.1	28.21	0.871	630.65	317.9
29.1	26.33	0.853	596.87	317.9
48.0	24.15	0.835	555.29	317.1
59.0	23.10	0.827	532.93	317.5
79.0	20.92	0.807	490.01	318.1
91.5	19.55	0.795	464.48	317.5
108.9	17.89	0.778	431.21	319.2

DISCUSSION OF RESULTS

It will be noticed that four liquids have been studied only at one temperature; viz.: bromine, phosphorus trichloride, diphenyl methane, and carbon disulphide. In the case of bromine, one temperature was considered sufficient owing to the fact that practically the calculated t_c agreed with observed one, and the Ramsay and Aston figures by aid of capillary rise, which disagreed with this, were stated by the authors to be inaccurate. With phosphorus trichloride at 60° difficulties were encountered, possibly due to the presence of water vapor in the air, although it was passed first through drying tubes, a yellow substance forming in the ventilation tube, and giving a slightly variable result, although the mean value agreed practically with that at the lower temperature which leads to practically the observed t_c and agrees with that found from capillary rise. With diphenylmethane at 23° it was impossible to get satisfactory results owing to the fact that it was below its melting point, and crystallization in the tube was hard to avoid, so that checking results at this temperature were difficult to obtain. Since the value of *tc* at 59° does not differ greatly from the value found by Dutoit & Friderich at 108°, it was thought more important to consider further liquids rather than continue work with this. Carbon disulphide was used here only to see what effect would be produced by the known purity of this sample, as compared to that purified in this laboratory.

Assuming, since in the case of bromine and phosphorus trichloride, the t_c calculated agrees with the critical temperature, and, in the case of diphenylmethane it is in agreement with that found at 108° by Dutoit & Friderich, that these liquids are non-associated, we can conclude that all of the liquids examined above, with the exception of dimethyl aniline, are non-associated, *for all,* with this exception, *lead to the same calculated value of* t_c (within a very small difference) *at both temperatures of observation.* In the case of dimethylaniline the same downward trend is shown by drop weight as is to be noticed from the results of capillary rise. It is probable however, that this discrepancy of 0.8% between 59.5° and 21.° is due to the decomposition of the liquid, for it darkens

very rapidly on exposure to light, and the low temperature observation was made first when the liquid was perfectly fresh. Possibly a reversed trend would be the case if observation at *high* temperature was made while the liquid was *fresh.*

The agreement of the calculated t_c with the observed critical temperature was found to be very satisfactory for the following liquids: brombenzene, bromine, ethylidene chloride, toluene, phosphorus trichloride, paraxylene, orthoxylene, metaxylene, while in mesitylene, ethylbenzene, and iodobenzene the discrepancies are below 1% for the former, and slightly above that for the two latter. For the other liquids the calculated t_c i. e., the fictitious critical temperature, viz. the point 6° below which, by the formula $f(M)=k_B\ (t_c-t-6)$, $f(M)$ would be zero, is larger than critical temperature for cymene, dimethyeaniline, ethylene chloride, methylaniline, ethylaniline, isobutylacetate and diphenylmethane.

It is possible to compare with these values of the calculated t_c, the corresponding values found from capillary rise, and consequently to find proof for the relationship

$$w : \gamma :: k_B : k'_B$$

for only the following liquids: carbon disulphide, cymene, dimethylaniline, diphenylmethane, ethylaniline, toluene, phosphorus trechloride, metaxylene, methylaniline, and mesitylene. In the cases of toluene and phosphorus trichloride the agreement is practically perfect between the critical temperatures from drop weight and capillary rise. With diphenylmethane, ethylaniline, cymene, and methylaniline, a value of *tc* at some temperature in capillary rise values is always to be found which is equal to the one constant at both temperatures by drop weight method. In the case of methylaniline, the large change from 9.09° to 108.5° when compared with the smaller one between 108.5° and 210.8° would seem to indicate error somewhere, which of course may be due to decomposition. With dimethylaniline the trend is the same in all results, although it can hardly be said that the agreement in the capillary rise values is satisfactory—all this, including the trend, may well be due to the decomposition of this liquid, which seems to be very unstable in pure condition. For cymene the mean of all values from capillary rise is 395.5, which agrees fairly well with the constant drop weight value of 394.7. For metaxylene the drop weight values are constant but lower than either set found from capillary rise, but the fact that capillary rise values do not even agree well enough with one another, indicates that there is a source of error in capillary rise in case of this liquid.

CONCLUSIONS

The results of this research may be summarized as follows:

I. According to the new definition of the normal molecular weight, i. e., that the normal (benzene) constant k_B gives for the liquid a constant value of t_c independent of the temperature of observation, in the relationship

$$f(M) = k_B (t_c - t - 6)$$

the following liquids are to be regarded as perfectly non-associated as is benzene itself: brombenzene, bromine, ethylidene chloride, toluene phosphorus trichloride, para-, ortho-, and meta-xylenes, mesitylene, ethylbenzene, iodobenzene, flourbenzene, cymene, ethylenechloride methylaniline ethylaniline, isobutylacetate, carbon disulphide, and diphenylmethane. In the case of dimethylaniline the discrepancy in the values of t_c is 0.8%, which is much too great for an experimental error, and can only show that the molecular weight is slightly abnormal, which could be due to the fact that the liquid is readily decomposed.

II. Of the values of t_c calculated for the above liquids, those for brombenzene, bromine, ethylidenechloride, toluene, phosphorus trichloride, ortho-, meta-, and para-xylenes agree excellently with the observed critical temperature; while the disagreement with this for ethylbenzene and iodobenzene is around 1%.

III. The agreement between the calculated values of *tc* from drop weight and those for capillary rise, with the 11 liquids which have been studied by that method is exceedingly good for toluene and phosphorus trichloride. In other cases the mean of the t_c from capillary rise agrees well with that from drop weight, and it is only for mesitylene and metaxylene that the values in mean from capillary rise disagree with those from drop weight. In the latter case, however, this seems to mean little, as the values by two observers, although higher throughout, do not agree even fairly with one another.

BIOGRAPHY

Garabed K. Daghlian was born January 11, 1882, in Aintab, Turkey. He graduated from Central Turkey College in 1902, spent the year 1906-7 in graduate study in Syrian Protestant College, Beiruit, Syria, and attended Columbia University as a graduate student in the faculty of Pure Science, 1909-1911. He received an M.A. from Columbia University in 1910, and was appointed University Scholar in Physical Chemistry for 1910-11. He was an assistant and instructor in Central Turkey College, 1902-1909.

twenty non-associated liquids